JOINT STOCK COMPANY
"HYPERSONIC SYSTEMS RESEARCH INSTITUTE"

EXPERIMENTAL RESEARCH OF THERMOCHEMICAL REACTORS
WITH COMBINED HEAT- & MASS- EXCHANGING SURFACES
FOR HEAT UTILIZATION & HYDROCARBON FUEL CONVERSION
IN VARIOUS POWER PLANTS
(SPC 98-4087)

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INTRODUCTION

Creation of hypersonic atmospheric aircraft needs to resolve a range of complex scientific technical problems. One of them is energetic problem. Original solution was proposed in the concept "AJAX" developed in holding company "Leninetz" (St. Petersburg, Russia) [1-3]. This concept is based on active energy interaction between a vehicle and air flowing around it. One channel of energy interchange is the system of active thermal protection. It is a combination of recuperative heat exchangers, which are placed in the most heat-stressed parts of airframe and engine. Various physical and chemical processes, from elementary heating of coolant to endothermic catalytic reactions, proceed there. The hydrocarbon fuel (aviation kerosene) is coolant and reactant, and utilized heat from aerodynamic heating and power plant is energy source for realization of physicochemical transformations. Thus, from the point of view of energetics, in difference from other designs "AJAX" flight vehicle utilizes fuller the primary energy, which is reserved aboard as chemical energy of fuel. It helps to increase the efficiency of thermodynamic cycle of the engine.

The considered heat-protection system executes not only usual function, providing temperature conditions of the airframe, but also serves simultaneously as the system of preparation of new modified fuel containing molecular hydrogen. It is a prominent aviation example of using the thermochemical conversion of hydrocarbon fuel on basis of the method of Chemical Heat Regeneration (CHR).

1. METHOD OF CHEMICAL HEAT REGENERATION

The present-day state of the heat power industry is characterized by the wide usage of the energy-saving technologies. The heat regeneration is the integral part of such technologies. This is one of possible ways to increase the efficiency of heat power devices.

The chemical way should be highlighted among various ways of the heat regeneration as the versatile one. The analysis of the functioning of numerous power devices shows that the efficiency of an organic fuel usage is still low and does not exceed 40%. For existing heat devices this situation may be explained thus: the fuel energy conversion is accompanied by large heat losses to the environment with the exhaust gases, the heat transfer through walls of devices, and the considerable irreversible losses during the process of the fuel burning. These losses could be considerably decreased by the utilization of previously lost heat in the special catalytic reactors (heat exchangers). In the process of the utilization, the initial organic fuel is converted into the new kind of the fuel, so-called synthetic gas (mixture of H_2 and CO). The comparative thermodynamic analysis of the process of the combustion of the initial and the converted fuels shows, that the quantity of irreversible losses is also lower in the last case than in the previous one. Therefore, the chemical heat utilization and the combustion of the converted fuel lead to the increase of the power plants efficiency and to the fuel save. Moreover, the synthetic gas combustion leads to the decrease of the pollutants emission into the atmosphere. That is why the process of the chemical heat regeneration is an example of the new energy-saving and environmentally friendly technology.

Various aspects of the usage of the CHR-method are versatile [4-8]. They include the utilization of the heat in heat power devices and in heat technological devices with simultaneous generation the hydrogen-containing fuel. They give a method of the heat protection of the structural elements, subjected to the action of large heat flows. At last, they give one possible method of the accumulation and transportation of the energy, generated in the solar and nuclear power stations.

While in traditional devices the energy of the fuel is converted into the heat in one stage by means of its direct combustion, in CHR-devices the process of the fuel energy conversion is divided into two stages. The first stage is the heat removal from the heated surface and realization of endothermic reaction of conversion of the initial fuel. The second one is the combustion of the reaction products (converted fuel) which have larger calorific value in comparison with the initial reactants.

It should be pointed out that the first stage has a fundamental interest as the method of the cooling (heat protection) of the heat-stressed structural elements. The heat protection is ensured not only by means of convection and radiation, but by means of the heat absorption at the phase transitions and chemical transformations also. At the same time, the latter do not have destructive character as in the case of ablative heat shield materials, but they are methods of generation of new fuel.

Development of thermochemical methods of the increase of the fuel utilization efficiency with simultaneous heat loss utilization requires the solution of the number of scientific and applied problems. They are outlined in the Fig. 1. There are three interconnected blocks of problems can be marked: 1) the choose of fuels and endothermic processes, the development of catalysts; 2) the development of heat-exchange devices, including thermochemical reactors (as design units of heat-protection system) and systems of fuel conversion; 3) the support of burning and the choose of scheme of combustion chamber with use of conversion products.
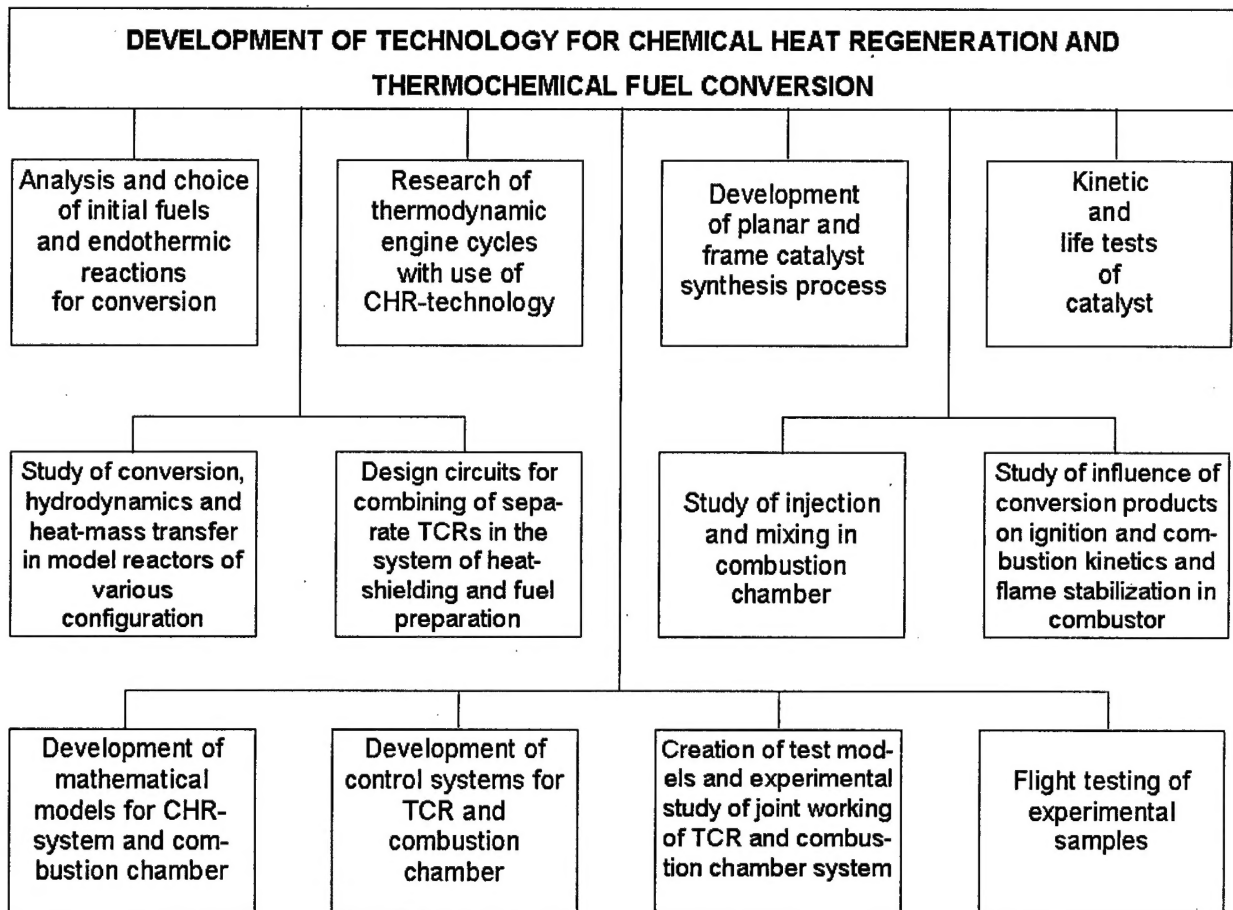
DEVELOPMENT OF TECHNOLOGY FOR CHEMICAL HEAT REGENERATION AND THERMOCHEMICAL FUEL CONVERSION

Analysis and choice of initial fuels and endothermic reactions for conversion	Research of thermodynamic engine cycles with use of CHR-technology	Development of planar and frame catalyst synthesis process	Kinetic and life tests of catalyst
Study of conversion, hydrodynamics and heat-mass transfer in model reactors of various configuration	Design circuits for combining of separate TCRs in the system of heat-shielding and fuel preparation	Study of injection and mixing in combustion chamber	Study of influence of conversion products on ignition and combustion kinetics and flame stabilization in combustor
Development of mathematical models for CHR-system and combustion chamber	Development of control systems for TCR and combustion chamber	Creation of test models and experimental study of joint working of TCR and combustion chamber system	Flight testing of experimental samples

Fig.1. Development stages

## 2. ENDOTHERMIC TRANSFORMATION OF HYDROCARBON FUEL

The question of fuel choosing for hypersonic flight vehicles of various purposes is, apparently, one of basic at development of hypersonic hardware. The properties of fuel in many respects determine the scheme and the performance of engine, and the design of vehicle as a whole at use of fuel for cooling of heat-stressed parts of apparatus.

In many designs of hypersonic flight vehicles, the liquid hydrogen is considered as a fuel. It has a number of unique properties such as large heat capacity, high mass-heat value and kinetic characteristics of processes of ignition and combustion etc. At the same time, liquid hydrogen, as an aviation fuel, has also a number of essential flaws. Small density and low boiling point (cryogenic features) are main ones. It results in necessity to place large fuel tanks with shield-vacuum isolation aboard an airplane that increases weight, sizes, drag, and worse lift-to-drag ratio. Besides, the changeover to liquid hydrogenous fuel will increase time of flight preparation of airplane and change completely the aerodrome infrastructure. Reasons of operational air safety and the economic indexes also speak for the benefit of hydrocarbons. Therefore, in parallel with the development of hydrogen-fuel projects of hypersonic flight vehicles, the ways for "life prolongation" of hydrocarbon fuels for hypersonic aircraft are under investigation.

Such capability is present if to try to subject hydrocarbon fuel to certain chemical transformations directly aboard a flight vehicle. It is possible to increase heat-absorption ability (cooling capacity) of hydrocarbon fuel using various endothermic reactions. That is why the term "endothermic fuel" came in literature. Usual aviation kerosene and synthetically created special hydrocarbon compounds can be used as such fuels. One of products of decomposition of hydrocarbons is the molecular hydrogen. It can improve the kinetic and ecological characteristics of basic hydrocarbon fuel at addition to it. So, by thermochemical conversions it is possible to increase significantly the heat-absorption ability of the initial fuel and to receive new high-quality modified fuel. These two circumstances allow still considering hydrocarbons as a likely fuel of the future hypersonic airplanes. Moreover, now many aviation specialists are inclined to believe that the non-cryogenic hydrocarbon fuel is the only possibility to provide super- and hypersonic speeds for flight vehicles of the limited size and small weight.

Amongst the existing endothermic reactions [9, 10] we consider the steam reforming. The choice was based on such reaction criteria as heat, temperature level, rate, grow of calorific value, amount of received hydrogen and some others.

Reaction heat exerts considerable influence on the heat quantity absorbed in the thermochemical reactor. Consider as an example the reaction of steam reforming of methane at stoichiometric relation between the components (CH_4 – 0,47 kg, H_2O – 0,53 kg).

$$CH_4 + H_2O = 3H_2 + CO - 207 \text{ kJ}$$
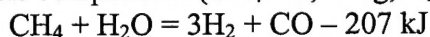
The change of enthalpy of initial reagents during the preparation stage (so-called physical cooling resource) is the result of heating, evaporation and superheating of methane-water mixture. This change is $\Delta H_{phys} = 3,3$ MJ/kg of mixture in the range from $t = 0$ deg C to $t = 727$ deg C. Chemical cooling resource, is equal to the reaction heat, $\Delta H_{chem} \approx 6,6$ MJ/kg of mixture. Thus, the total cooling resource $\Delta H_\Sigma = \Delta H_{phys} + \Delta H_{chem} = 9,9$ MJ/kg of mixture.

The cooling capacity of liquid hydrocarbons/water mixture falls insignificantly when amount of carbon atoms in molecule grows. By and large it is possible to consider that methane and its liquid homologes mixed with water are capable to provide cooling capacity up to 8-10 MJ/kg of mixture. For comparison, the change of enthalpy of liquid hydrogen heated to temperature of autoignition ($t = 577$ deg C, $\Delta t = 830$ deg C) is equal to $\Delta H_{phys} = 12$ MJ/kg. Thus, hydrocarbon/water composition comes nearer to the case of cooling by liquid hydrocarbon on available cooling capacity, and outperforms that case on relative cooling capacity $\Delta H/H_u$ (H_u is the heat of combustion). This circumstance and also high potential (exergy) of received gaseous fuel allow to view application of hydrocarbon fuels with thermochemical conversion for realization of cycles, which will outperform the Brighton's cycle used traditionally in air-breathing engines [11].

It is necessary to note that the catalytic steam reforming of hydrocarbons exceeds by thermal effect and amount of received hydrogen in some times the non-catalytic endothermic processes such

as pyrolysis, cracking and depolymerization of hydrocarbon. The complexity is in making the developed heat-exchange catalytic surface and maintenance of its properties during all time of work.

Concrete form for reaction of steam reforming depends on the process conditions (temperature, pressure, relation between water and hydrocarbon, and others). Therefore, at high temperatures ($t > 1000$ deg C) the reactions go until the formation of H_2 and CO (high-temperature reforming):

$$aC_nH_m + bH_2O \rightarrow fH_2 + gCO \tag{1}$$

At low temperatures (t < 400 deg)   the reaction output is strongly shifted to the formation of $_4$ and $_2$ and the resulting reaction of gasification can be written as (low-temperature reforming):

$$aC_nH_m + bH_2O \rightarrow dCH_4 + eCO_2 \tag{2}$$

Generally, reactions (1) and (2) are accompanied by two additional independent reversible reactions, which determine equilibrium composition of converted gas:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{3}$$
$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{4}$$
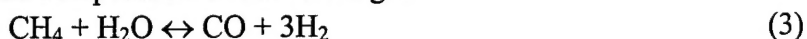
Unfortunately, the process of hydrocarbon decomposition is complicated by undesirable reactions of free carbon (coke) formation that leads to the coking of catalysts. The coke, depositing on the catalyst surface, deactivates the catalyst blocking its active centers. In addition, the coke, clogging the pores, causes the destruction of catalyst at the expense of difference in coefficients of expansion. We considered in detail the following ways to decrease the coking:

a) appropriate choice of initial fuel;

b) promotion of catalysts;

c) exceeding of stoichiometric relation $_2$ / ;

d) efforts on rational organization of the process (for example, two-stage scheme of decomposition, optimal shape of catalysts, elimination of local temperature inhomogeneities etc.);

e) use of special fuel additives;

f) regeneration of catalyst.

It is known [12] that the rate of coke deposition on surfaces of nickel-containing catalysts reduces in the order ethylene > benzol > heptane > hexane > butane > methane. And the ratio of C/H in the methane molecule is minimum. Thus if the raw material is methane, carbon deposit formation is not a critical problem. From this comes the conclusion that it is necessary to organize the process of dissociation of the initial liquid hydrocarbon (kerosene) in such a manner that in the most crucial, largest surface area, and most inaccessible places of heat-shielding construction, the conversion would involve gaseous methane. Such arrangement is possible at using a two-stage system for the steam reforming of liquid hydrocarbons (Fig. 2). In such system, the process occurs in two steps. First, liquid hydrocarbons are gasified at low temperature ($t = 300\text{-}450$ deg C) via the reaction (2). In the second step, the products of gasification are transformed according to the reactions (3), (4) in a high temperature ($t = 700\text{-}900$ deg C) conversion step. This scheme of the working process has several advantages compared to a single-step scheme. For high-temperature conversion we use the gas mixture consisting of methane that is stable to coke formation, carbon dioxide and small amount of hydrogen, damping the cracking reactions. As a result the danger of coking the catalyst is substantially reduced. This scheme also gives possibility to reduce the excess of water vapor in the conversion process and to approach stoichiometry relation between the initial components.

The scheme of two-stages process given at Fig.2 is simplified, becoming one-stage scheme at the following conditions: (i) the initial fuel is methane; (ii) the working time is not large and then the coke formation is negligible. In both cases the immediate high-temperature steam reforming is efficient.
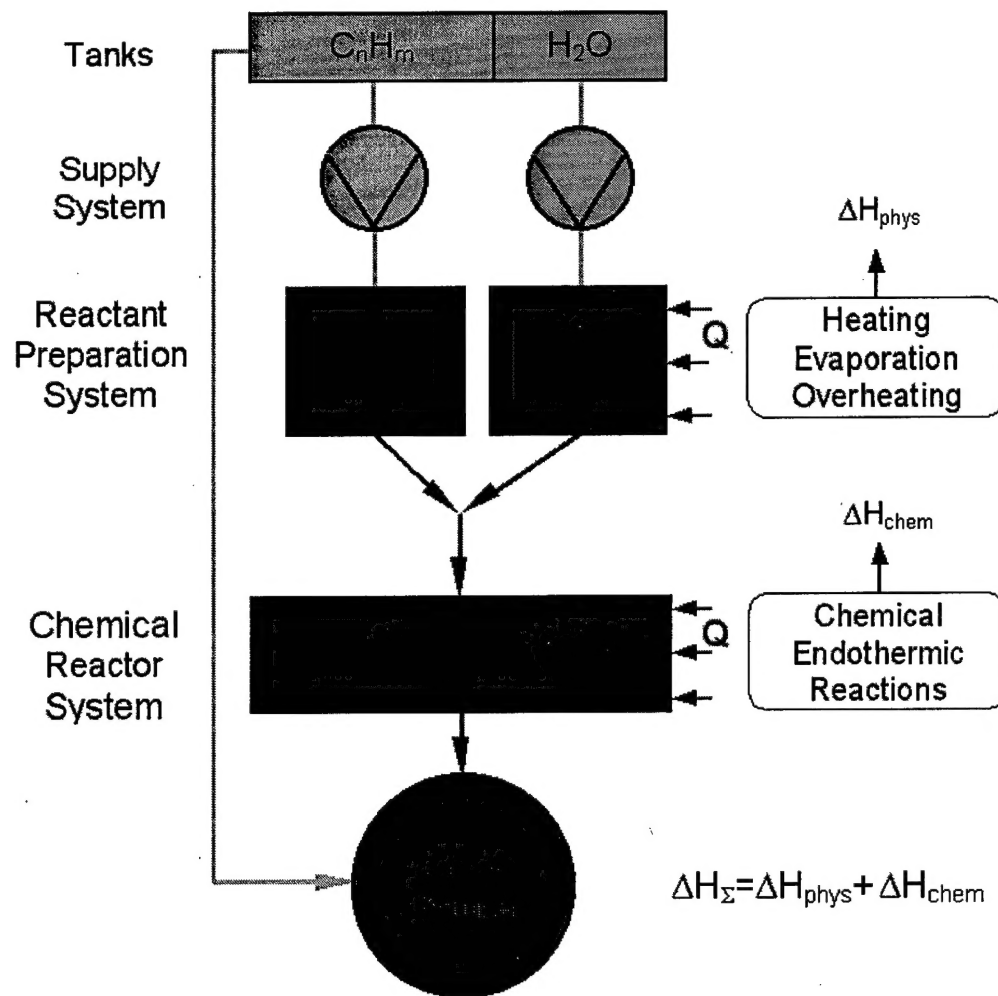
Tanks

Supply
System

Reactant
Preparation
System

ΔH_{phys}

C_nH_m H_2O

Q Heating
Evaporation
Overheating

ΔH_{chem}

Chemical
Reactor
System

Q Chemical
Endothermic
Reactions

$\Delta H_{\Sigma} = \Delta H_{phys} + \Delta H_{chem}$

Fig.2. Scheme of working process aboard hypersonic flight vehicle

3. HEAT REMOVAL FROM CATALYST SURFACE

The gaseous heat-carriers, in which the endothermic chemical reactions take place at heating, attract attention as high-temperature heat-transfers agents having potentially high cooling ability. The use of gas, that reacts chemically, as a coolant is promising for two factors. Firstly, the effective heat capacity of the gas increases considerably at the expense of the heat effect of the endothermic reaction; therefore, the heat release from the surface being cooled can be increased considerably when the temperature of the cooling gas is increased to the same extent. Secondly, the heat exchange process in the chemically reacting gas incorporates common convective heat transfer with diffusive transmission of the latent heat of the reaction; in contrast to convective heat transfer, the latter does not create considerable temperature differences. Therefore, when both types of heat transfer act in parallel at the boundary layer, the overall heat transfer at the cooled wall increases considerably.

The consideration of thermochemical principle of cooling with using endothermic catalytic reactions has resulted in necessity to conduct analysis of heat removal efficiency in limits connected to substance and heat transferring. This work was done by Institute of Catalysis [10] and Institute of High Temperatures [13] on our proposition.

In [10] the influence of diffusion limitations of the rate of catalytic thermochemical reaction on heat flow from the surface of catalyst was discussed. More than 13 often used endothermic reactions was analyzed. The theoretical analysis has been developed on the base of the equation of multi components diffusion of gases and experimental laws for processes of mass exchange in the packed beds. The kinetic equations has been taken from literature.

It was shown, that the reactions can be divided in two groups: low temperature reactions, that in practice can be carried out until 900 K and high temperature reaction up to 1200 K.

For the low temperature reactions maximal heat flows Q take place at steam reforming of methanol (at degree of conversion 0.3 $Q = 0,4 \, MW/m^2$). For high temperature reactions the decomposition of ammonia $(Q = 0,9 \, MW/m^2)$ and the steam reforming of methane $(Q = 0,75 \, MW/m^2)$ can be recommended for high heat removal.

In contrast with [10] the authors [13] have created the technique of the computational analysis for processes of heat- and mass-exchange in porous catalytic coating in view of heat-transfer through the frame of coating. The model of a heated wall with catalytic coating, scheme of heat- and mass-exchange process and the local values of heat flows are shown on Fig.3. Technique of calculation is founded on the joint solution of two equations:

$$\lambda_P \left(1 - P\right) \frac{d^2 T}{dy^2} = q_V, \qquad \rho D_1 n \frac{d^2 c}{dy^2} = j_{1V},$$

where λ_P is the effective value of thermal conductivity of the porous coating, P the porosity, q_V the volume intensity of the internal heat sink, j_{1V} the volume rate of the reaction, D_1 the effective coefficient of the methane diffusion in the coating pores.

The received estimations allow to conclude that in the relatively long reactors the level of the heat flow rates which can be expected at the acceptable for the high-temperature steels wall temperatures and at the moderate initial pressures of the order 0,3-0,5 MPa is of $(0,8 \div 1,2) \cdot 10^6 \, W/m^2$. The higher values are achieved in shorter reactors. The calculations show also that the microporous coatings with the thickness $L = 10^{-2} \text{-} 10^{-3}$ mm, the pores diameter $d_P = 10^{-4} \text{-} 10^{-6}$ mm, and the thermal conductivity λ_P not less than 1 W/(m·K) are the most effective.

It is interesting to note that despite of different physical gears included in computational models [10, 13] they give the same value on an order of magnitude for removed limit heat flow ($q \sim$ 1 MW/sq. m.) at a degree of conversion $X = 20\text{-}40\%$. And q falls when X increases, that is explained, partially, by dilution of initial mixture by reaction products.
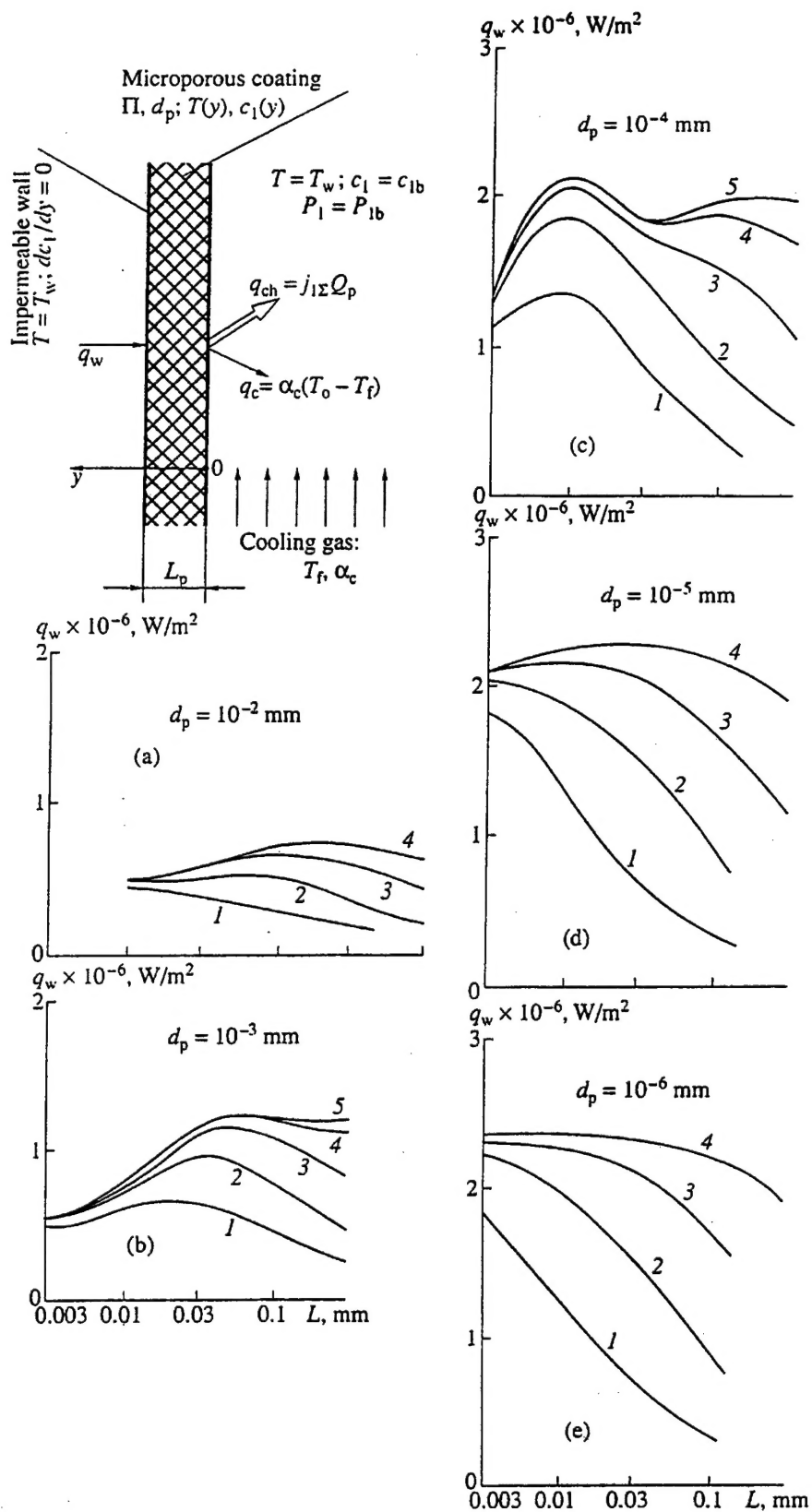
Fig. 3. The model of a heated wall with a microporous catalitic coating; scheme of the heat-and-mass transfer process and local heat flow rates with T_W=1200K as a function of the thickness and thermal conductivity with a porosity of Π=50% and different diameters of the pores. p_0 = 0.3 MPa, c_{10} = 0.376, α_c=1150 W/(m²K); T_f = 800K; λ_p, W/(m K): (*1*) 0.2; (*2*) 1.0; (*3*) 5; (*4*) 25; (*5*) 125.

4. ONBOARD CATALYSTS FOR CONVERSION OF HYDROCARBONS

As is generally known, the process of steam reforming of hydrocarbons is a basic industrial method to produce technical hydrogen. It is carried out in tube furnaces, which are heated on the outside and filled with granular catalytic packing. The bulk catalyst has very large contact surface; however this surface works ineffectively because along its way from the heating wall, which is essentially non catalytic, to the surface, where catalysis takes place, the "chemical" component of the heat flux has to overcome a series of thermal resistances: a) from the heating wall to the gas, b) from the gas to the granule surface with gas flowing over it, and c) from the surface to the pores that are located inside the granules. Thus, in this case, convective and diffusive head transfer do not occur in parallel (this is favorable for resultant enhancement of heat transfer, as was pointed out above); on the contrary, these processes take place sequentially, that is, from convective to diffusive heat transfer. As a result, the temperature at the granule surface, which determines the chemical reaction on the average, appears to be considerably lower than that for the heating wall; that is, the effect of the chemical reaction on the intensity of heat transfer at the heating wall is much less then it could be.

Besides, practically all reactors with fixed granular layer have the following defects: significant radial gradients of temperatures and concentrations; a low degree of using catalyst volume; high hydraulic resistance of granule layer; irregularity on altitude of mechanical loading on catalyst [14].

The use of granulated catalysts aboard flight vehicle is undesirable generally, as at mobility of reactionary space the granule propensity to migration and repacking will only grow, that will cause to intense friction and crumbling of granules. Therefore it is necessary to have new approach to creation both catalysts, and units of conversion in whole to increase intensity of catalytic processes in industry, and also develop new CHR technology for heat machines of various purposes.

Besides the traditional requirements imposed on the activity, selectivity and life time, the onboard catalysts should satisfy several specific conditions, such as: (i) they should be integrated with the heat transfer surface; (ii) they should have high thermoconductivity, and thermocyclic, shock, vibration, and chemical-heat resistance; (iii) they should operate under the action of time-dependent and large magnitude heat flows. To satisfy these requirements we considered a series of new "know-how" of catalysts, such as deposited catalytic coatings and sponge layers on metal ware with any shape, and volumetric frame catalysts. The latters are the metal basis made of high porous cellular material which is coated by cermet coating (the carrier of $Cr_3C_2 - NiO - Cr_2O_3$ kind), active component (Ni) and promoters (γ-Al_2O_3, BaO, MgO) [15]. Porosity of catalyst layer is 85-90% and the size of frame cell is 2-3 mm. Open porosity of cermet coating – 40-55%, specific surface – 15 sq. m./g, pore mean size – 0,05-0,1 micrometers. The catalytic activity of frame catalyst was estimated on a degree of methane transformation. The experiments were done in the quartz reactor with diameter of 30 mm with isothermal zone size about 100 mm. The catalyst as a set of cylinders of 15 mm height was loaded into this zone. The experiment results are shown in Fig.4. It is visible, that at volumetric speed $w = 1700$ h^{-1} the degree of methane transformation is close to equilibrium in all interval of temperatures. With increase of volumetric speed the degree of transformation is reduced, that can be connected with partial methane overshoot through layers of catalyst. The experiments were done at a ratio $H_2O/C = 2$. The maximum activity of catalyst at $t = 800$ deg C is stayed through 20 min after beginning of supply of steam-methane mixture. The loss of activity after 50 hours was about 2%. The coke deposition was not observed visually.

High porous frame catalysts (Fig.5) considered above can serve as the fillers for channels of any shape. Such channels have low hydraulic resistance, and the good heat conduction of frame attached rigidly to wall provides proportional heat distribution in volume. The sectional view of two model reactors with frame catalyst is shown in Fig.6.
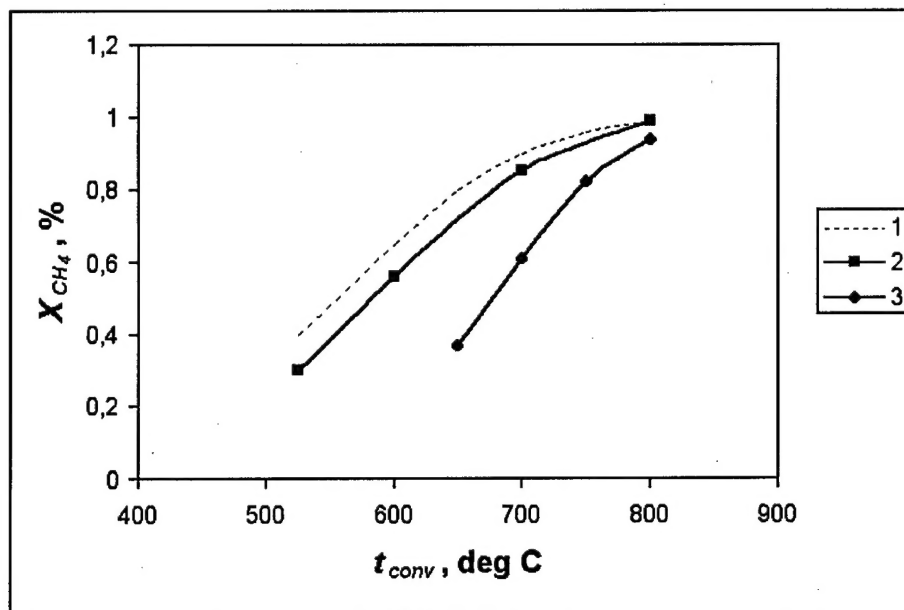
Fig. 4. Relation of methane conversion degree from temperature at ratio of $H_2O/C=2$:
1: equilibrium curve; **2**: $\omega = 1700$ h^{-1}; **3**: $\omega = 3500$ h^{-1}
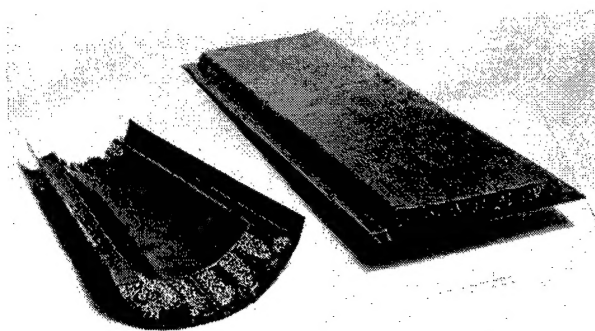

Fig.5. Examples of high-porous catalysts

Fig.6. Fragments of model reactors

However at all virtues of frame catalysts first of all it is necessary that the heat-conducting wall was catalytic active. The so-called planar catalysts serve for this purpose. They can be produced by deposition of carrier and active component on defended wall or by formation of spongy layer, using wall material. Baldi-Damiano technology described in [16] can be an example of the latter technology. We suppose this technology is very promising, but nowadays for producing CHR catalytic coating, we use gas-thermal deposition method described in [17]. It includes next stages: preparation of tube surface to deposition; deposition of sublayer; deposition of basic coating; quality surveillance of a product. For increase strength of coupling of the coating with basis the surface for deposition is subjected to jet-abrasive processing by corundum with the grain size of

0,5-1,0 mm at pressure of compressed air 0,5-0,6 MPa. The deposition of sublayer is made by chrome-nickel powder with thickness of 0,05 mm with use of nitrogen plasma. The basic coating by thickness of 0,15 mm is made by the powder of same composition with the grain size 20-100 micrometers by flame spraying in oxidizing environment. Gas-thermal deposition by powder materials allows producing coatings having porous structure, what is characteristically for heterogeneous catalysts. At open porosity of 20-30%, the effective mass-exchange inside the catalytic coating is provided. At the same time the soldering of particles form a strong frame ensuring thermal cyclical strength (>80 thermal cycles) and high effective heat conduction. Oxide films on the nickel particles surface after reduction in hydrogen flow create a secondary microporous structure with specific surface up to 20 sq.m./g. According to [14] catalytic activity of Ni-Cr coatings, made on described above technique, is commensurable with activity of industrial catalyst (developed by Institute of Nitrogen Industry) for steam reforming of methane. Relation of CH_4 conversion degree from effective velocity of process W_{eff} is shown in Fig.7. Here $W_{eff} = V_{CH_4}/F_K$, where V is the volumetric gas flow-rate, F_K the geometric active surface of catalyst. The experiments were done in the electric-heated reactor with internal diameter of 21 mm. The cylindrical reactionary element with Ni-Cr coating on lateral surface of diameter 17 mm at wall temperature 900 deg C was coaxial inserted inside the reactor. During the 20-hours test of Ni-Cr catalysts at ratio $H_2O/CH_4 = 2$ the deactivation caused by coking was not observed.

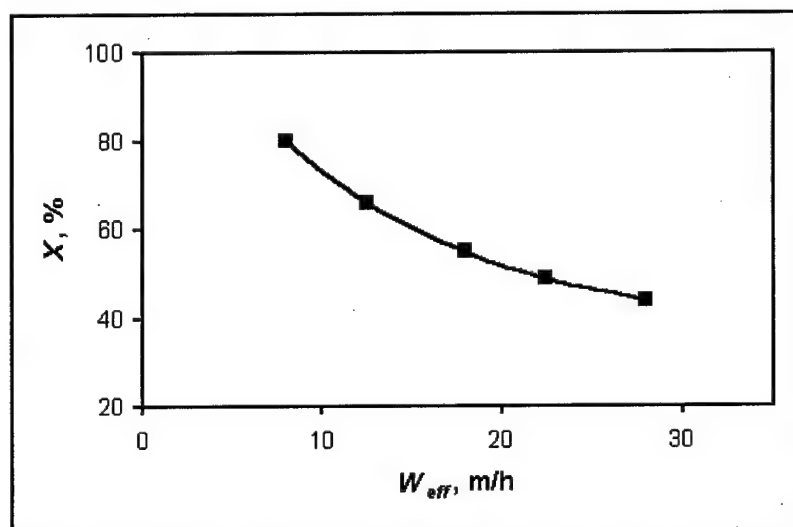Fig.7. Relation between CH_4 conversion degree X and the effective velocity W_{eff}.
$W_{eff} = V_{CH_4}/F_K$, V is the volumetric gas flow rate, F_K is the geometric active surface of catalyst

5. TEST STAND FOR THERMOCHEMICAL REACTORS

Methane was selected as one of reactants in the considered reaction at the thermal testing of thermochemical reactor (TCR). This choice is not random; it is dictated by technological features of offered system of heat protection. As noted above, heat-shielding reactors is fed by gas mixture based on methane. The gas mixture is the product of gasification of an initial liquid hydrocarbon aviation fuel (kerosene, for example) in the auxiliary device. Methane and water are the initial reagents for hydrogen producing. Steam reforming of methane has maximal heat-absorbing effect and minimal tendency to the coking.

The installation for steam reforming of methane (Fig.8 a-c) is intended for:

– experimental investigation of the thermochemical reactor operation under the action of stationary and non-stationary heat flows with the aim of determination of the limit value of the heat absorption, operating characteristics of TCR and the process data of the steam reforming;

– search for the optimum constructions and technology of the TCR manufacturing with use of planar and frame catalysts, and means of intensification of the heat- and mass exchange.
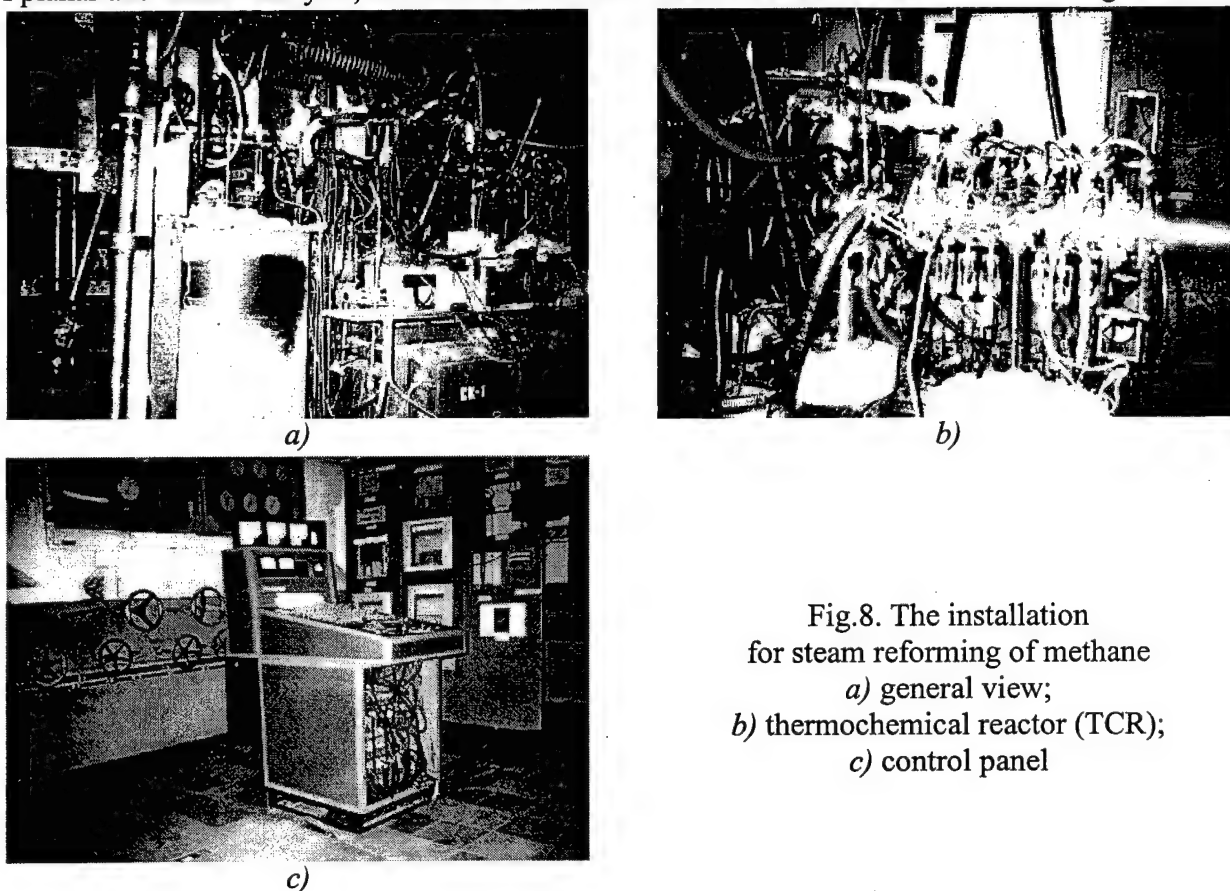

a)

b)

c)

Fig.8. The installation
for steam reforming of methane
a) general view;
b) thermochemical reactor (TCR);
c) control panel

The schematic diagram of the installation is shown in Fig.9a.

The principal parameters of the installation are:

– the methane flow rate – up to 5 g/s;
– the steam flow rate – up to 15 g/s;
– the pressure in TCR – $0,2 \div 2$ MPa;
– the temperature at the TCR inlet – $773 \div 973$ K;
– the maximum temperature of the TCR wall – 1173 K.

The cylinder slot channel having the length 450 mm and the clearance 2 mm formed by two coaxial cylinders is the main assembly of the installation for methane steam reforming (Fig.9b.) The internal surface of this cavity is covered with the catalyst. The chemically reacting methane/steam mixture is fed into the cavity. The heat input is realised through the internal wall from the high temperature nitrogen jet fed from the controlled power arc plasma heater with output upper limit of

200 kW. The choice of such heater is dictated by the necessity of the heat input of the order of hundreds of kilowatts at the small operating volume of the cavity. The mass-averaged temperature of nitrogen can reach 5000 K in this case.
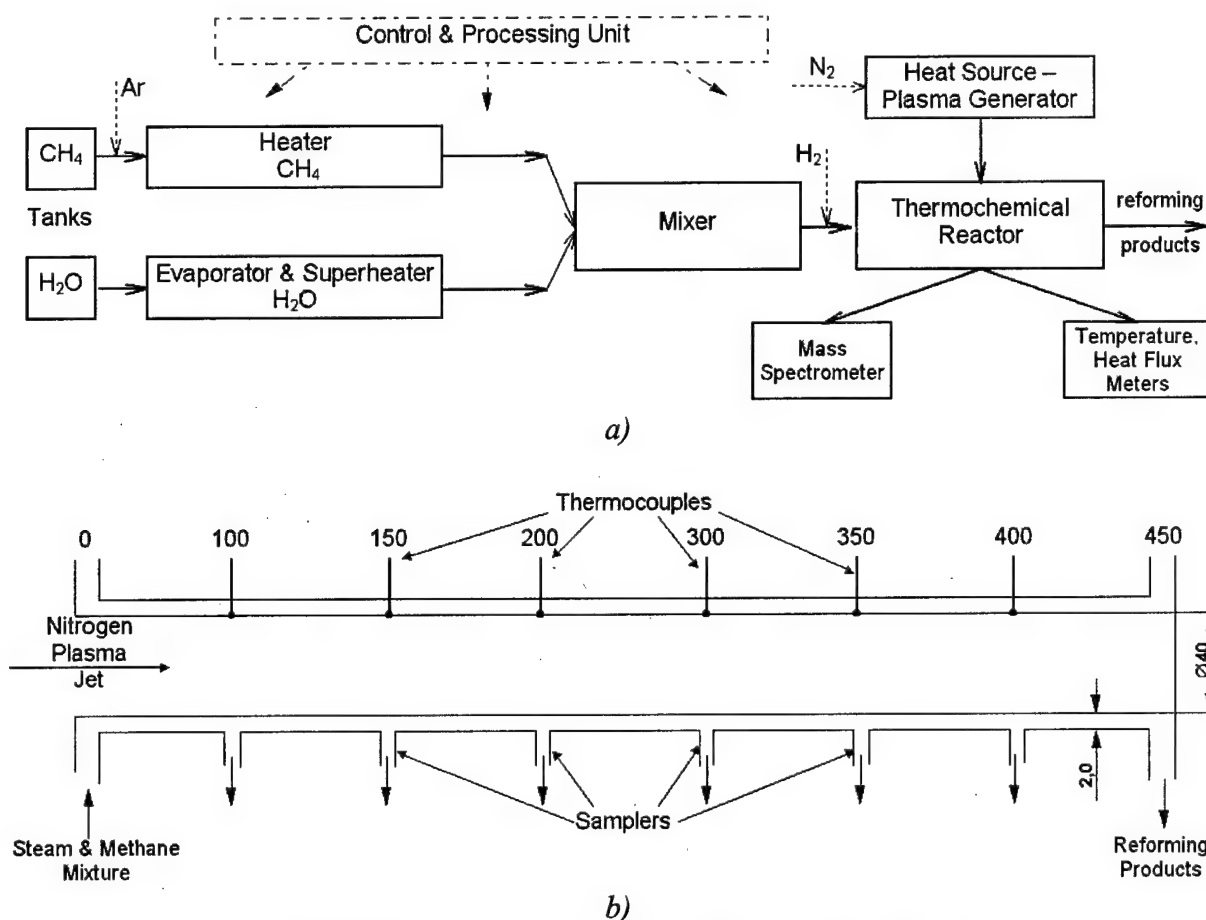

a)

b)

Fig.9. The installation for steam reforming of methane
a) diagram of the installation; *b)* scheme of channel

Measuring of the temperature distribution along the internal wall of the slot duct is provided by chromel-alumel thermocouples.

The sampling tubes of the reforming products for mass-spectrometric analysis are located in the cross-section of the operating channel where the mentioned thermocouples are placed. The sampling is realized through the usual and shut-off valves into the special sample containers. These containers are evacuated by the vacuum pump before the experiment. They can be disconnected from the device and can be connected to mass-spectrometer.

To keep the given operation thermal mode automatically, there is a special control system, connected with the power supply system of the arc heater. Stabilization of predetermined temperature level of the most heated initial area of the working channel is maintained automatically for every investigated mode of the reaction.

The distilled water is forced out of the water container by nitrogen at the pressure up to 15 atm and is delivered to the evaporator. Steam is generated in the device composed of two main units: the water evaporator and the steam superheater. The evaporator is the steel container of internal volume 40 litres with thick walls and the resistance heating element. The maximum power of the heater of the evaporator is 14 kW. From the evaporator the steam is carried to the coil pipe where it is overheated to required temperature by the electric current. The described device allows to control with sufficient accuracy the steam flow rate, which is determined only by the input electric power and by the heat loss into the environment. The latter having been measured and for their decrease the outer surface of the evaporator is covered by the thick layer of the heat insulator.

The methane heater is the coil tube heated by the resistance element. The tube has internal diameter 9 mm, the wall thickness 2,5 mm and the total length 7000 mm. The maximum power of the methane heater is 4 kW.

The methane-steam mixture is fed into the slot channel of the TCR through two holes tangentially. That provides the homogeneous distribution of the mixture in the starting part of the channel. The constructions of the TCR and facilities for the production of the steam-gas mixture are hermetic and are made of the stainless steel.

To prepare TCR to the working state the reduction of the catalyst is carried out in the hydrogen flow with the rate of 50 g/h and the temperature of 600 deg . The blow-through the system before the work and the conservation of the catalyst after the experiment is carried out with the neutral gases Ar or N_2.

The experimental set-up is supplied with process instrumentation to provide the measurement and control such parameters of the steam, methane, gas-steam mixture, nitrogen and hydrogen as temperature, pressure, flow rate, gas composition, and others. The correspondent transducers are connected to the computer installation to provide automatic measurement and processing of the experimental data according to the developed software.

6. MEASUREMENT AND CALCULATION PROCEDURES

Temperature

The temperatures of reactor walls and used hot gases were measured by chromel-alumel thermocouples with recording of the indications on an automatic potentiometer. The statistical characteristics of thermocouples were defined before experiments by method of comparing of the indications on the researched thermocouple with the exemplar thermocouple at various temperatures of its working tip and fixed temperature of free tips. The maximum checking error at maximum temperature 1200 deg C is ±5 deg C. The total measurement error of temperatures of the wall and steam-methane mixture in view of an error of the device is estimated as ±7 deg .

Steam flow-rate

In all conditions, the steam flow-rate in active channel of the facility is only determined by the electric power fed to the evaporator, and by thermal losses into environment. To reduce the losses the exterior of the evaporator is coated with a thick layer of thermal insulation made from "keramzit" (expanded clay).

The thermal losses can be estimated with the help of expression:

$$Q_n = \left(c_{stainless} \, m_{stainless} + c_{Cu} m_{Cu} + c_{H_2O} m_{H_2O} \right) \left(dt/d\tau \right)_{\tau=0}, \tag{1}$$

where $m_{stainless}$ and m_{Cu} are masses of the evaporator details made from stainless steel and copper; m_{H_2O} the mass of water in the evaporator; $c_{stainless}$, c_{Cu}, c_{H_2O} the heat capacities of stainless steel, copper and water at $t = 100$ deg C; $\left(dt/d\tau \right)_{\tau=0}$ the time gradient of the temperature, that corresponds to the moment when the heater of the evaporator is just turned off.

The assessment of thermal losses in the evaporator was made with the help of Eq.1. All details of the evaporator were weighed. To determine $\left(dt/d\tau \right)_{\tau=0}$ the special experiments were done. During the experiments, the change of water temperature was fixed depending on cooling time, since a moment of the heater cutoff; in doing so, the vessel neck was closed.

With the help of the received relationship $t = f(t)$ the gradient of temperature at the first moment of cooling $\left(dt/d\tau \right)_{\tau=0} = -0,0071$ deg/s was found. The value of thermal losses $Q_n = 0,311$ kW was calculated by Eq.1.

The relation between the electric power of the evaporator and the steam flow-rate is displayed in Fig.10.
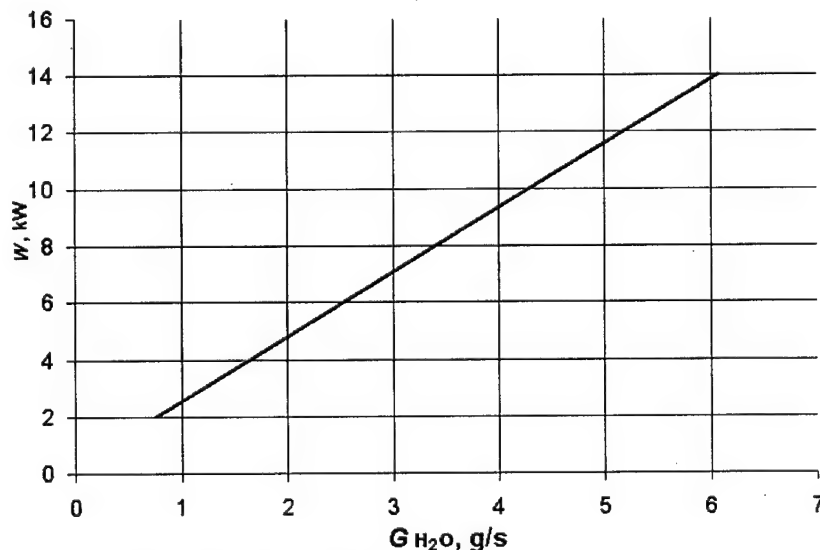

Fig.10. Relation between the electric power of the evaporator W and the steam flow-rate G_{H_2O}

Methane flow-rate

To achieve stable fixed methane flow-rate we used the convergent nozzle with the local sound speed reached in the nozzle throat. The mass gas flow-rate in the nozzle throat is determined by the following equation:

$$G = f(k)PF\sqrt{RT/M} , \qquad (2)$$

where F is the area of the nozzle aperture, $f(k)$ the known function of gas adiabat k, P the total gas pressure in the chamber before the nozzle, T and M are temperature and molar gas mass correspondingly, and R is the universal gas constant.

The described procedure of measuring of the flow-rate was also tested by immediate calibration of the nozzle with the help of the gas counter and has shown the reliability. The error of measurement of gas flow rate does not exceed ± 2 %.

Flow-rate and linear velocity of steam/methane mixture

It is obvious, that the mass mixture flow-rate is equal to the sum of mass flow-rates of methane and steam: $G_{mix} = G_{CH_4} + G_{H_2O}$.

According to known expression for mass flow-rate:

$$G_{mix} = \rho_{mix} V_{mix} S ,$$

it is possible to determine the linear velocity of mixture V_{mix} in the reactor inlet. Here $\rho_{mix} = 1 / \sum_i^n \dfrac{m_i}{\rho_i}$, m_i and ρ_i are the mass fraction and the density of components respectively at given temperature in the reactor inlet, S the area of the reactor section.

The gas analysis

The analysis of gas samples taken during the experiments was performed in laboratory on mass-spectrometric installation, which includes a magnetic mass spectrometer and the system of sampling into an ionic source of this device. The scheme of mass-spectrometric device is shown in Fig.11.
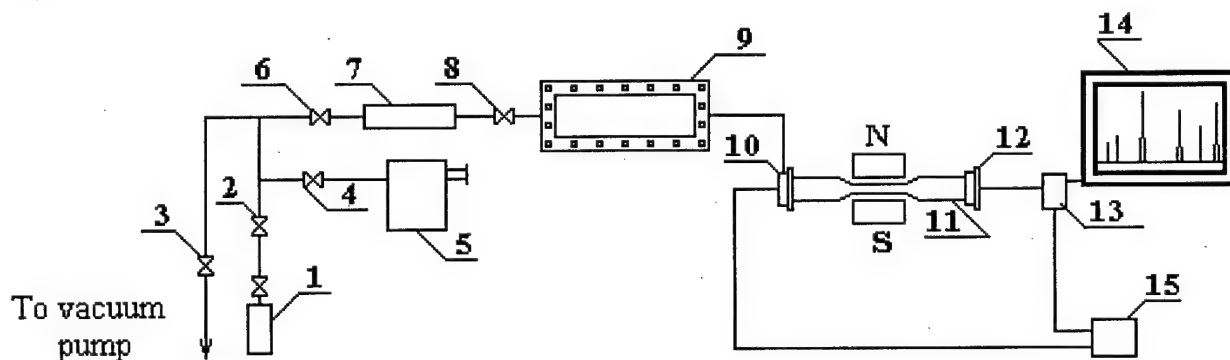

Fig.11. Scheme of the laboratory mass-spectrometric device

Main elements of the sampling system are the mercury manometer (5), capacity of adjusted volume (7) and gas admission cylinder (9).

During the analysis on mass-spectrometric installation, gas sample goes from sampler (1) into capacity (7). Then, gas from this capacity bypasses into the gas admission cylinder (9). From the cylinder, the gas through an aperture in the thin diaphragm falls in an ionic source of the mass spectrometer. It consists of the following units:

– source of ions (10);
– chamber-analyzer (11);
– devices for ion reception and registration, and for the measuring of intensity of ion current for each component (12-14).

Besides the units listed above, the spectrometer also includes vacuum system with pumps and electronic circuits of power supply and control for operating mode of the device (15).

The natural gas conversion products leaving the reactor of the test facility contain H_2, CO_2, CO and CH_4 as main constituents. To determine the contents of these components in gas samples at quantitative analysis the factors of sensitivity for each component in relationship to the one, accepted as "the internal standard", were previously determined. Hydrogen was selected as the standard. The factors of sensitivity for CO_2, CO and CH_4 were determined in relationship to hydrogen. These coefficients are listed in Table 1.

Table 1

Component	2	2	CO	4
Relative factor of sensitivity	1,00	4,38	4,17	3,30

At the quantitative analysis, it was necessary to take into account that during the ionization of $_2$ by the method of electron impact, besides molecular ions with m/e 44 (CO_2^+) there are also formed fragments with m/e 28 (CO^+) and m/e 16 (O^+). During the recording of mass-spectrum the intensities of the specified fragments are superposed on intensities of molecular ions of corresponding masses with m/e 28 (CO) and m/e 16 (CH_4); these ions are also in gas samples.

To take into account this superposition the mass-spectrum of $_2$ w a s measured separately and the relative structure of fragments CO^+ and O^+ was determined in relationship to primary molecular mass-spectrum with m/e 44. These data were subsequently used at the quantitative analysis of structure of conversion products. This analysis was executed in the following order:

1. The mass-spectrum registration was done in the range of masses between m/e 44 and m/e 15 for each gas sample. In doing so, the intensities of peaks corresponded to molecular ions H_2, CO_2, CO and CH_4 were measured.

2. The correction for background presence in the device was entered. The hum was measured before the start of research of sample containing conversion products.

3. At processing of the received mass-spectra the corrections for superposition of intensities of fragments formed at ionization $_2$ and intensities of peaks appropriated to molecular ions with m/e 28 (CO^+) and with m/e 16 (CH_4^+) were entered.

4. To account the factors of sensitivity for main components in relationship to hydrogen the correction was added.

5. The sum of intensities of molecular peaks for components H_2, CO_2, CO and CH_4 was determined.

6. Relying on the received results the concentrations C_{CO_2}, C_{CO}, C_{CH_4} and C_{H_2} were determined.

7. Based on the received values C_{CO_2}, C_{CO} and C_{CH_4} the degree of conversion of methane was calculated under the formula:

$$X = \frac{C_{CO_2} + C_{CO}}{C_{CO_2} + C_{CO} + C_{CH_4}} \cdot 100\%.$$

Heat flux calculation

To calculate the heat flux fed from the nitrogen jet to reactionary zone it is necessary to determine a heat-transfer coefficient of the nitrogen jet to TCR wall and to calculate the thermal resistance of the reactor wall determined by the finite value of thermal conductivity of wall material. According to [19] the dimensionless heat-transfer coefficient is:

$$Nu = 0{,}021\, Re^{0{,}8}\, Pr^{0{,}6},$$

where $Re = 2r\dfrac{G_N}{\pi r^2 \mu}$, r is the radius of the internal cylinder of the reactor, G_N the nitrogen mass flow-rate, μ_N the dynamic viscosity and Pr is Prandtle number for nitrogen at given jet temperature. Local heat-transfer coefficient is

$$\alpha = Nu \cdot \lambda_N / 2r,$$

where λ_N is the coefficient of thermal conductivity for nitrogen. Nitrogen jet temperature T_j in the reactor inlet can be calculated with high accuracy under the known working characteristics of plasma generator. Iterative procedure on the method of successive approximations was used for the registration of thermal resistance of the wall. According to this procedure as zero approximation starts, that temperature value on boundary "nitrogen – wall" T^0_{j-w} is equal to the temperature value measured on boundary "wall – steam/methane mixture" T_{w-mix}. Heat flux removed from the nitrogen jet is calculated as:

$$q^0 = \alpha \left(T_j - T^0_{j-w} \right)$$

We can calculate the gradient of temperature ΔT on the known thermal conduction of the wall and its width. After that the temperature value on boundary "nitrogen – wall" is corrected as $T^1_{j-w} = T^0_{j-w} + \Delta T$ and the heat flow q^1 in the following approximation is calculated. This iterative process fast converges and the obtained solution allows to determine the required value of heat flow fed from the nitrogen jet to steam-methane mixture.

The preliminary measurements have shown that the value of heat flow transferring into the reactor wall varies along the reactor. Because of it the essential errors can be obtained if to calculate the heat flow on the wall temperature averaged on the reactor length and to assume the temperature of nitrogen jet is constant on all length. Therefore the step procedure is used for calculations of heat flow. According to this procedure the reactor is divided into a number of the comparatively short sections on length. On each section the heat flow is calculated and the falling of temperature of nitrogen jet because of outflow of heat into the wall is taken into account. On each next section the calculations are executed on the basis of new (smaller) value of mass-average temperature of nitrogen. Such approach provides possibility of more exact calculation of an integral heat flow (on all reactor wall area). In particular, it is possible to investigate in detail areas with maximal and minimal heat flow etc.

7. THE RESULTS OF THE EXPERIMENTS

In this section the results of the experiments on steam reforming of methane are presented. The experimental conditions were as follows:

$H_2O/CH_4 = 2$;

the temperature of steam/methane mixture at the reactor input is about 550 deg C;

the maximal temperature of the reactor wall is no more than 950 deg C;

the mixture velocity at the reactor input is 1-5 m/s.

The experimental data are registered at the attainment of a quasi-stationary working mode of the experimental installation, when the basic parameters of the process are invariant. The time it takes to establish the working mode after the start of the installation is not less than half-hour; a switching to another temperature takes 10 min.

The distribution of temperature of the internal wall of the reactor at neutral gas (nitrogen) supply in the reaction area, i.e. in absence of chemical reaction, is shown in Fig.12. If to exclude end effects, uniform pure-convective heating of nitrogen in the range between 100 and 300 mm is observed . The jet of plasma generator cools down, the gas in the reactor heats up. The distribution of temperature of the internal wall of the reactor is changed with supply of steam/methane mixture in the reactor input and in the course of inner chemical heat-absorbing reaction   (Fig.13). Heat absorption in catalytic centers of the reaction and the change of the mixture composition and its thermal properties along the length of the reactor, firstly, lead to the delaying of growth of the wall temperature, and subsequently cause the drop of the wall temperature (L=100-350 mm). The intensive course of the reaction on specified length is seen well in Fig.14, 15. These pictures represent the degree of methane conversion and the distribution of concentrations of methane and hydrogen along the reactor length, respectively.
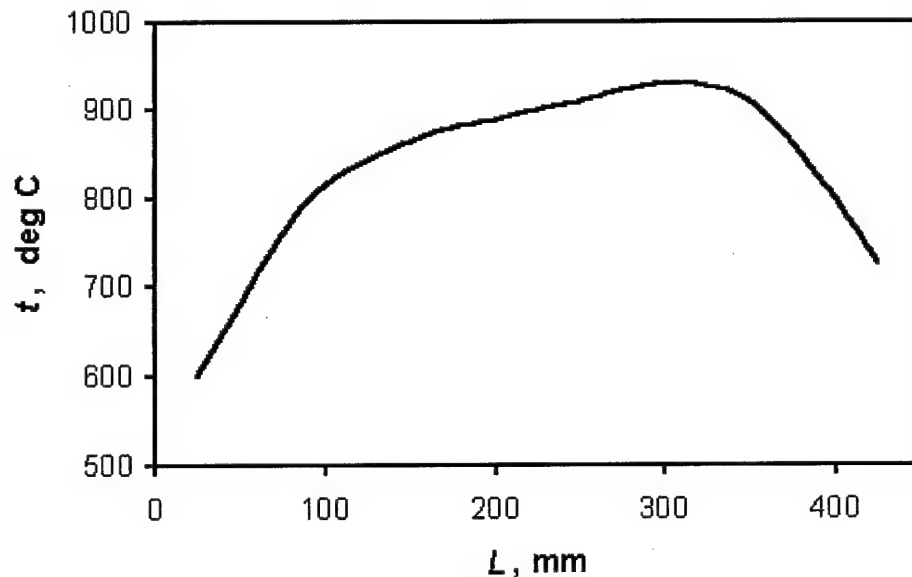
Fig.12. Temperature distribution along the reactor length at nitrogen injection
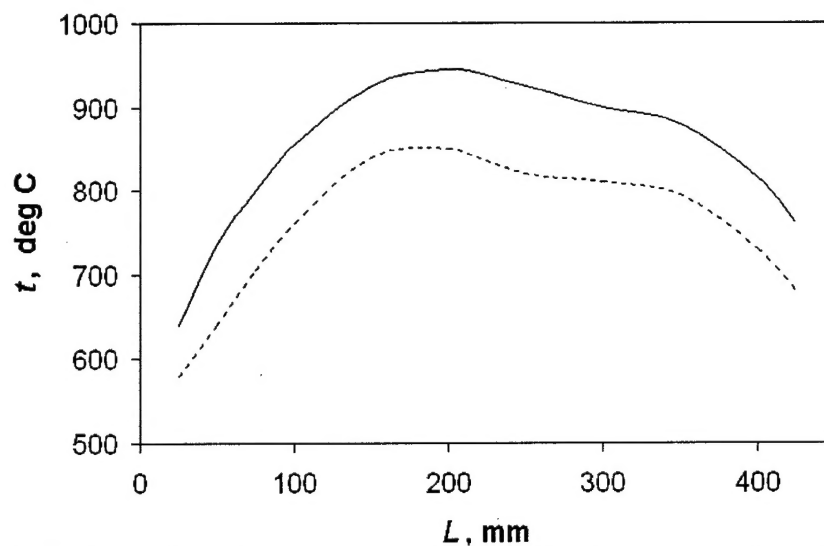
Fig.13. Temperature distribution along the reactor length (for two values of maximal temperature) at injection of steam/methane mixture
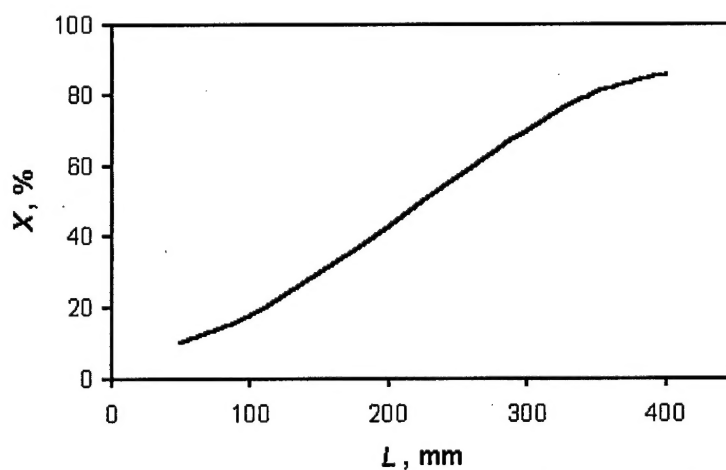

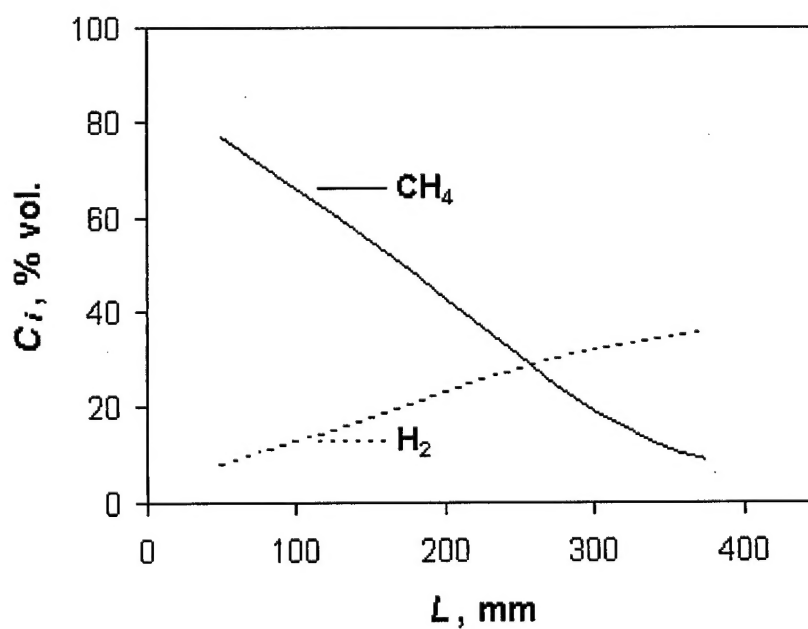Fig.14. Degree of methane conversion along the length of reactor

Fig.15. Concentrations of methane and hydrogen along the length of reactor

The relations between the degree of methane conversion X and the heat flux density averaged along the length of the reactor and the velocity of steam/methane mixture at the reactor input are shown in Fig.16, 17. The data of different days of experiments were taken randomly and averaged. The tendency of decrease of degree of conversion with the increase of the mixture velocity, and the insignificant growth of mean density of heat flow are visible.
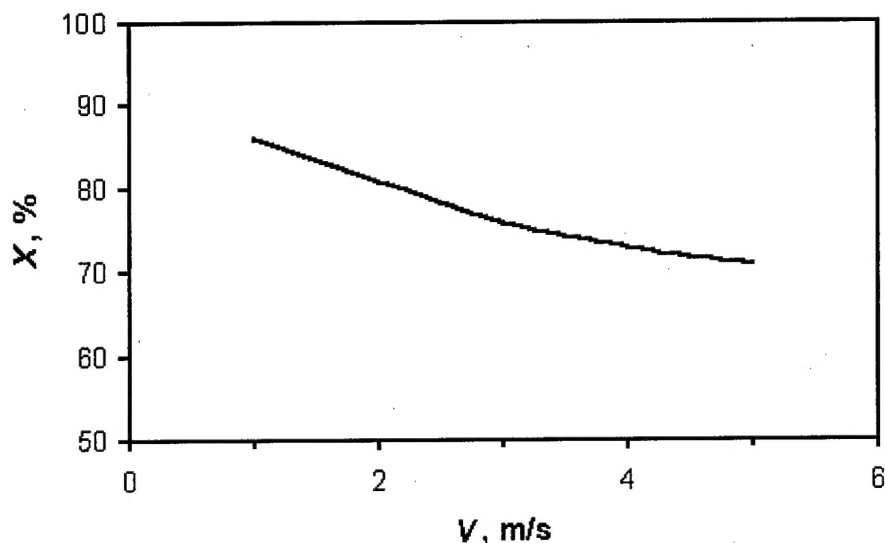

Fig.16. Degree of conversion X vs. mixture speed V at the reactor input
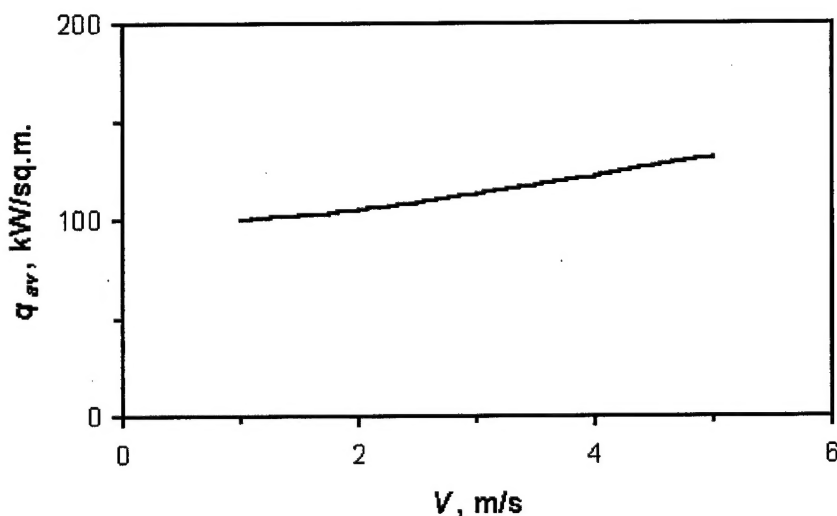

Fig.17. Mean density of heat flux q_{av} vs. mixture speed V at the reactor input

A comparison of results of this set of experiments with the experiments made earlier by us at high speeds of flow it is possible to note the following. First, when the feed of the mixture falls from $V_{mix} = 10$ m/s to $V_{mix} = 1$ m/s, the degree of methane conversion X grows from 30% to 85%. It is explained by increase of a residence time of reactant in the reactor. Second, the increase of the mixture feed within the specified limits leads to the increase of mean density of adsorbed flow in 3-4 times. This effect can be caused by the increase of probability of an event of the chemical reaction at relative decrease of quantity of the reagent, and also by redistribution of roles between "chemical" and convective components of adsorbed heat flow. These effects require to run special experiments for further research.

Generalizing the results of industrial use of methane steam reforming and the laboratory researches of this process at non-limited heat input, it is possible to make a conclusion about a possibility of thermochemical conversion of an initial fuel in a system of reactors with various degrees of conversion (10-100%) at heat utilization in a broad range of heat loads (0,05-1 MW/m^2).

In closing it may be said that the successful development of the considered technology is impossible without a close "feed-back" with its "consumers". The products of conversion of hydrocarbons include such combustible components as H_2, CH_4, CO; their contents can vary within wide range of limits depending upon the working mode of reactor. The fuel properties in turn determine the scheme, workability, and efficiency of a power plant in many respects. Therefore, in experiments on combustion of hydrocarbon fuels with the additives of conversion products, it is very important to determine the requirements to their optimal composition in reactor output and reactor productivity. The feedback can seriously affect technological development of reactors and catalysts. It is necessary to continue the works on this direction.

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